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Cure Schedule Evaluation of SC15 and SC79 Low-Viscosity Epoxy VARTM Resins

by Robert Jensen, Aaron Forster, Jessica Dibelka, and Craig Copeland

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Robert Jensen, Aaron Forster, Jessica Dibelka, and Craig Copeland
Weapons and Materials Research Directorate, ARL

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14. ABSTRACT
In this technical note, the effect of different cure paths on the ultimate glass transition temperature (T_g) and fracture toughness of Applied Poleramic SC15 and SC79 VARTM resins are studied.

15. SUBJECT TERMS
SC15, SC79, VARTM, cure schedule

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1. Introduction

Vacuum-assisted resin transfer molding (VARTM) is a manufacturing process to create fiber-reinforced composite parts in a fast and cost-effective fashion.[1, 2] This process uses vacuum pressure to infuse a low-viscosity liquid thermosetting resin (epoxy) through a woven fiber preform. This methodology is advantageous because composites are fabricated at higher fiber volume ratios than wet lay-ups and do not require the high-autoclave pressures of prepreg processing. There are several criteria required of an epoxy resin used in the VARTM process. Resins that have a viscosity below 1000 cPs and have long work times are required to insure wetting and flow through the woven fabric, which enables a low void content in the final cured composite part. Low-temperature curing epoxies (<250 °F) are of particular interest to the manufacturers of multicomponent composites. A lower curing temperature resin reduces residual stress in the final part, minimizes energy costs for curing, and reduces the effects of coefficient of thermal expansion mismatches between dissimilar materials that can concentrate stresses at bonding interfaces. Therefore, VARTM resins can involve complicated mixtures of components that include reactive diluents, additional reactants, and soluble rubber tougheners. The resins often exhibit multiple cure paths and the dominant cure path is dependant on the cure protocol followed. In this technical note, the effect of different cure paths on the ultimate glass transition temperature (T_g) and fracture toughness of Applied Poleramic SC15 and SC79 are studied.

2. Experimental

The resins under investigation are the SC15 and SC79 commercial VARTM resins developed by Applied Poleramic Inc. (Benicia, CA). These low-viscosity, epoxy-based resins are both rubber toughened, with SC15 having a lower ultimate T_g than SC79. Resins were cured according to the cure schedules often encountered in a manufacturing environment and are listed in table 1. Neat resin bars were made for differential scanning calorimetry (DSC) analysis and fracture toughness measurements. The fracture toughness (critical strain energy release rate, G_{IC}) was measured using an Instron 4505 according to ASTM D 5045-95.[3] The samples were prepared using the Single Edge Notched Beam geometry with a crosshead rate of 10 mm/min.

[1] Seemann, W. H. Plastic Transfer Molding Techniques for the Production of Fiber Reinforced Plastic Structures. U.S. Patent 4,902,215, 1990.

[2] Hsiao, K. T.; Gillespie, J. W.; Advani, S. G.; Fink, B. K. Role of Vacuum Pressure and Port Locations on Flow Front Control for Liquid Composite Molding Processes. *Polymer Composites* **2001**, 22, 660–667.

[3] ASTM D 5045-95. Standard Test Methods for Plane-Strain Fracture Toughness and Strain Energy Release Rate of Plastic Materials. Annu. Book ASTM Stand. **1995**.

Resin samples were mixed in a ratio of 100 g of epoxy to 30 g of hardener for SC15 and 100 g of epoxy to 40 g of hardener for SC79, per the manufacturer recommendations. The uncured resin was degassed in a vacuum to remove air bubbles and poured immediately into silicone rubber molds. The molds were covered with PTFE tape and placed into a converted, programmable gas chromatograph oven. Each set of fracture toughness and DSC samples were exposed to set pre-cure and post-cure conditions according to the following schedule (see table 1).

Table 1. Curing schedules for SC15 and SC79 resins.

Pre-Cure Conditions	Post-Cure Conditions
30 hours at 25 °C	No post-cure
24 hours at 25 °C	2 hours at 122 °C
24 hours at 25 °C	6 hours at 122 °C
24 hours at 25 °C	8 hours at 122 °C
24 hours at 25 °C	2 hours at 177 °C
24 hours at 25 °C	8 hours at 177 °C
2 hours at 60 °C	2 hours at 122 °C
2 hours at 60 °C	6 hours at 122 °C
2 hours at 60 °C	8 hours at 122 °C
2 hours at 60 °C	2 hours at 177 °C
2 hours at 60 °C	8 hours at 177 °C
No pre-cure	4 hours at 122 °C
No pre-cure	4 hours at 177 °C

After curing, the bars were allowed to cool slowly to room temperature (3.3 °C/min) to minimize residual stress buildup. For the DSC measurements, samples weighing ~10–15 mg were placed into aluminum crimped pans. The samples were ramped from 0 to 225 °C at a rate of 10 °C/min through two cycles. The T_g of the resin was determined using the half height method in the TA Universal Analysis software from first heat, second heat and cool down. The critical-stress-intensity factor (K_{IC}) and critical strain energy release rate (G_{IC}) at a span (S) to width (W) ratio of 4 are defined by the following expressions:

$$G_{IC} = \frac{(1-\nu^2)K_{IC}^2}{E}, \tag{1}$$

where

$$K_{IC} = (PBW^{1/2})f(x), \tag{2}$$

$$f(x) = 6x^{1/2}\frac{[1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)]}{(1+2x)(1-x)^{3/2}}, \tag{3}$$

and

P = load,
B = sample thickness,
W = sample width,
a = crack length,
x = $0.45 < a/W < 0.55$,
E = modulus, assumed 2.0 GPa for SC15 and SC79, and
ν = Poisson's ratio, assumed 0.35 for SC15 and SC79.

3. Results

Tables 2 and 3 show the tabulated results for the cure schedule study of SC15 and SC79.

Table 2. Tabulated results for the cure schedule study of SC15.

Pre-Cure Conditions	Post-Cure Conditions	1st Heat T_g (°C)	2nd Heat T_g (°C)	G_{IC} (J/m^2)
30 hours at 25 °C	No post-cure	44	NA	NA
24 hours at 25 °C	2 hours at 122 °C	82	97	2020 (±230)
24 hours at 25 °C	6 hours at 122 °C	NA	NA	NA
24 hours at 25 °C	8 hours at 122 °C	89	98	1430 (±100)
24 hours at 25 °C	2 hours at 177 °C	91	99	1460 (±240)
24 hours at 25 °C	8 hours at 177 °C	95	99	1320 (±210)
2 hours at 60 °C	2 hours at 122 °C	82	97	1920 (±240)
2 hours at 60 °C	6 hours at 122 °C	NA	NA	NA
2 hours at 60 °C	8 hours at 122 °C	87	97	1520 (±120)
2 hours at 60 °C	2 hours at 177 °C	88	97	1610 (±190)
2 hours at 60 °C	8 hours at 177 °C	93	99	1180 (±70)
No pre-cure	4 hours at 122 °C	86	97	1400 (±120)
No pre-cure	4 hours at 177 °C	90	100	1600 (±230)

Note: NA = not available.

Table 3. Tabulated results for the cure schedule study of SC79.

Pre-Cure Conditions	Post-Cure Conditions	1st Heat T_g (°C)	2nd Heat T_g (°C)	G_{IC} (J/m^2)
30 hours at 25 °C	No post-cure	44	NA	NA
24 hours at 25 °C	2 hours at 122 °C	116	156	285 (±61)
24 hours at 25 °C	6 hours at 122 °C	134	169	157 (±43)
24 hours at 25 °C	8 hours at 122 °C	137	161	173 (±32)
24 hours at 25 °C	2 hours at 177 °C	140	165	294 (±43)
24 hours at 25 °C	8 hours at 177 °C	176	179	413 (±61)
2 hours at 60 °C	2 hours at 122 °C	121	119	787 (±251)
2 hours at 60 °C	6 hours at 122 °C	109	121	523 (±18)
2 hours at 60 °C	8 hours at 122 °C	126	120	191 (±67)
2 hours at 60 °C	2 hours at 177 °C	151	161	290 (±115)
2 hours at 60 °C	8 hours at 177 °C	172	171	212 (±135)
No pre-cure	4 hours at 122 °C	139	169	227 (±124)
No pre-cure	4 hours at 177 °C	149	175	341 (±44)

Note: NA = not available.

4. Discussion

The following conclusions can be drawn from the T_g and fracture toughness results shown in tables 2 and 3:

1. The fracture toughness of SC15 is increased in comparison to SC79, regardless of cure conditions.

2. For room-temperature curing only, the T_g of SC15 and SC79 is 44 °C. For room-temperature cure conditions, both epoxies vitrify prior to achieving a significant degree of chemical conversion.

3. The ultimate T_g of SC15 is ~100 °C, which is below the post-cure temperatures of 122 and 177 °C of this study. Optimal high degrees of conversion in epoxy resins are typically achieved by selecting a post-cure temperature that is greater than the ultimate T_g of the resin, as vitrification of the epoxy prior to full conversion is avoided during cure. As a result of the high post-cure temperatures, SC15 achieved a T_g fairly close to 100 °C, regardless of the post-cure conditions used for this study.

4. The ultimate T_g of SC79 is ~180 °C, which is above the post-cure temperatures of 122 and 177 °C of this study. From the T_g data presented in table 3, it can be implied that SC79 vitrifies during cure. Vitrification into a glassy state occurs as the T_g of the epoxy continues to increase during cure. If the cure temperature is below the ultimate T_g, then eventually the increasing T_g will equal the cure temperature. At this point, the epoxy will vitrify, which essentially quenches further crosslinking reactions in the epoxy due to mobility restrictions. From this study, it can be seen that the T_g of SC79 typically increases with increasing post-cure temperatures and times, with the exception of the 60/122 °C pre- and post-cure conditions. As mentioned in the introduction, VARTM resin may involve complex formulations of reactive diluents to decrease processing viscosity. The mixtures of reactants could have varying chemical reaction mechanisms and rates. At the 60/122 °C pre and post-cure conditions, SC79 locks in a first heat DSC T_g of approximately 120 °C that is not increased upon further cure. For all other pre- and post-curing conditions, the second heat DSC T_g increases, which is a typical response for classic epoxy systems. Unlike SC15, the higher ultimate T_g of SC79 and formulation variations result in a resin system with increased sensitivity to curing conditions.

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